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New Developments in Ultracapacitor Technology

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FUZES BRANCH
MUNITIONS DIVISION

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The objective of this in-house research project is to develop new high surface area (HSA) electrodes suitable for use as primary internal components of ultracapacitors. Ultracapacitors are low voltage charge storage devices that do not involve chemical reactions to store or release energy; instead, planar HSA electrodes are employed to hold charge across a thin layer of electrolyte. In the past, ultracapacitor development has relied heavily upon use of exotic electrode materials (i.e., platinum group metal oxides) which are stable in aqueous sulfuric acid electrolyte. Ultracapacitor availability has been hindered by the lack of more common substitute electrode materials, such as HSA molybdenum nitride, which possess adequate electronic conductivity and also offer equivalent long term compatibility with the electrolyte.

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PREFACE

This report describes an in-house effort conducted by personnel of the Fuzes Branch (MNMF), Munitions Division (MNM), Wright Laboratory, Eglin Air Force Base, Florida, under exploratory development project funds.

The work reported herein was performed during the period 7 June 1993 to 30 December 1994, under the direction of Dr Duane Finello (WL/MNMF), project engineer.

The author wishes to thank Mr Scott Roberson for preparation of electrodes in support of the subject experimentation. Ruthenia electrode material furnished through courtesy of Pinnacle Research Institute (Los Gatos CA) is also gratefully acknowledged.

NEW DEVELOPMENTS IN ULTRACAPACITOR TECHNOLOGY

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New Developments in Ultracapacitor Technology

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INTRODUCTION

Development of more sophisticated weapons has brought about the need for more compact, highly reliable energy sources. Requirements for advanced electronic fuzing have supported development of the ultracapacitor, an energy storage device employing planar high surface area (HSA) electrodes to hold charge across a thin layer of electrolyte. Having demonstrated virtually unlimited rechargeability, the versatility of the ultracapacitor as a power source has opened up a number of concurrent commercial applications.

Perhaps most crucial to widespread acceptance of ultracapacitor technology is the development of new types of electrodes and electrolytes. Traditionally, mixed metal oxides containing platinum group elements have been the basis for the technology. It was once thought that semiprecious metals were required for HSA oxide layer growth. A better understanding of nonequilibrium nucleation theory has been applied to demonstrate that molybdenum nitride, for instance, can be formed as HSA electrode material using molybdenum trioxide as the precursor. It is important that non-corrosive electrolytes offering much higher cell voltage than aqueous electrolytes can be used successfully with a wide variety of electrodes.

Ultracapacitor device availability has been greatly aided through joint efforts of PRIDCO (Los Gatos CA) and Westinghouse-Gould (Cleveland OH). Automated mass manufacturing has begun for devices of various sizes to address several main applications. Continued commercial market growth is expected to coincide with future improvements in device design.

SECTION II

EXPERIMENTAL PROCEDURES/RESULTS

It was conjectured that the molybdenum nitride work accomplished by Jaggers[1] might be extended for ultracapacitor electrode fabrication. Using identical preparative procedures, it was attempted to determine whether or not HSA molybdenum nitride could be made from supported HSA molybdenum trioxide in such a way that it becomes permanently bonded to the support substrate. Titanium metal foil was the substrate material chosen since it is commonly used for electrode fabrication. For convenience, oxide-to-nitride conversion using ramp heating ammonia treatments to 700 degrees C were accomplished in one hour rather than several hours prescribed by the above reference.

Ultracapacitors were fabricated from pairs of 1 cm x 1 cm electrodes (each with a 1 cm tab to facilitate clip lead attachment) separated by Whatman filter paper to prevent shorting during charge and discharge tests. Two types of electrolytes were used: 1) nitromethane plus potassium iodide and 2) aqueous sulfuric acid of 32 percent concentration by weight. The electrode pairs were held together in vertical position using a rubber band and a pair of Pyrex microscope slides. With electrode tabs pointing upwards, the ultracapacitor assembly was placed in a zip lock bag containing a small amount of electrolyte which was able to wick up the filter paper but could not reach the copper clip leads. (The electrolyte would become contaminated and would have to be discarded if it came into contact with either of the copper clip leads.)

Protected by a current limiting resistor, a coulometer was used to measure the capacitance of the specimen. The specimen was first connected to a constant voltage source (0.5 volt) for 5 minutes to enable it to equilibrate to a stable charge. Then it was disconnected from the source and connected to the coulometer to measure the amount of charge stored in units of coulombs. A Princeton Applied Research Model 379 Digital Coulometer protected with a 10-ohm current limiting resistor was used for charge measurement. Capacitance (in units of farads) was calculated readily since it simply equals the charge stored (in coulombs) divided by the charging voltage. The results of several ultracapacitors using molybdenum nitride electrodes are compared with a ruthenia mixed metal oxide standard of identical size (see Table 1).

SAMPLE	ELECTROLYTE	CHARGE IN COULOMBS	VOLTAGE IN VOLTS	CAPACITANCE IN FARADS
7-JY-94	NITROMETHANE	0.054	.5	.11
	H2S04	0.165	.5	.34
19-JY-94	NITROMETHANE	0.054	.5	.11
	H2S04	0.165	.5	.34
20-JY-94	NITROMETHANE	0.068	.5	.14
	H2S04	0.262	.5	.53
29-JY-94I	H2S04	0.180	.5	.36
29-JY-94T	H2S04	0.217	.5	.44
RUTHENIA	H2S04	0.377	.5	.75

Table 1. Capacitance measurements for several molybdenum nitride based ultracapacitors as compared with mixed metal oxide* ruthenia standard.

*Sample courtesy of Pinnacle Research Institute (Los Gatos CA)

SECTION III

DISCUSSION

The data resulting from this study indicate that molybdenum nitride can be made in HSA form in such a way as to remain bonded to titanium foil substrate material. The molybdenum nitride (Mo_2N) compares favorably with ruthenia mixed metal oxide electrode material with regard to conductivity, capacitance, corrosion resistance, and ease of application yet the raw materials are inherently much more plentiful and would not discourage high volume ultracapacitor production.

Ultracapacitors for hybrid electric vehicles will undoubtedly require use of aqueous sulfuric acid electrolyte for optimum ionic conductance. The added expense of the electronic control systems for efficient power management becomes extremely prohibitive when nonaqueous electrolytes are used (despite the higher cell voltages possible) due to reduced ionic conductance by approximately two orders of magnitude. Efforts with molybdenum nitride/aqueous sulfuric acid ultracapacitor systems will continue to attempt to validate a methodology to ensure long term performance comparable to that offered by the traditional ultracapacitor.

For applications which do not require optimum power density, it is possible to achieve increased energy density through use of nonaqueous electrolytes offering higher cell voltages. Lithium perchlorate/propylene-ethylene carbonate and methide based liquid salts[2] are examples of electrolytes that can approach 5-volt cell operation and hold considerable promise for future ultracapacitor designs. However, a substantial increase in the average pore size of the electrode coating may be required to facilitate more rapid charging and discharging of such devices. Hermetically sealed cells of rolled electrode internal construction can be envisioned which may someday compete with rechargeable batteries in some applications.

SECTION IV

CONCLUSIONS

Over the past several years, it has been evident that ultracapacitor availability has been greatly restricted by the lack of a mass manufacturing system capable of reducing unit cost. Westinghouse-Gould and PRIDCO have made great strides in this area, but customers involved with huge markets must still question the long-term supply of ruthenium and the dependency upon the mixed metal oxide electrode.

An alternative ultracapacitor electrode has been presented, perhaps along with a more reasonable philosophy. The question of "What makes an oxide more suitable than a nitride?" is certainly worth pondering, especially if the nitride is stable with regard to oxidation over the voltage range of interest and if the device is sealed to discourage entry of external oxygen. HSA nucleation and growth theory is capable of being further developed, and we claim that a wide variety of materials can be grown with greatly increased surface area. The main concerns from an ultracapacitor electrode application standpoint are that the HSA coating material be highly conductive, corrosion resistant (with respect to the electrolyte over the electrochemical operating range), and viable with regard to cost. Molybdenum nitride has fairly high potential in each of these areas, and it is anticipated that this new development will facilitate mass manufacture of new devices which will result in continued growth of new ultracapacitor markets.

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1. C. H. Jaggers, PhD Thesis, University of California, Berkeley, 20 Dec 1988 (UMI order number 8916713).

2. L. A. Dominey, U.S. Patent No. 5,273,840, 28 Dec 1993.

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